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Relative Solubility of RDX and TNT in Supercritical CO_2

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Abstract

Mixtures of 2,4,6-trinitrotoluene (TNT) and the nitramines cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) are used in a variety of high-explosive formulations, such as Composition B (RDX/TNT) or Octol (HMX/TNT). There has been much recent interest in the use of supercritical fluid (SF) CO_2 technologies for the processing and/or demilitarization of energetic materials. The solubility of RDX in neat CO_2 was measured over a temperature and pressure range of 303–353 K (30°–80° C) and 6.9–48.3 MPa (1,000–7,000 lb/in^2) and is presented in this report.

RDX was found to be relatively insoluble in neat CO_2 in the temperature and pressure range studied, with a maximum solubility of about 0.25mg/g of CO_2. Data for TNT solubility in CO_2 have recently been published by a group of researchers at the Fraunhofer Institut für Chemische Technologie. Consideration of the relative solubilities of RDX and TNT in CO_2 suggests that SF extraction (SFE) of TNT should be effective for separation and recovery of nitramine materials from TNT-based energetic formulations. RDX is found to be 2-3 orders of magnitude less soluble than TNT in SF CO_2. An SFE-based separation process is demonstrated on a synthetic mixture of RDX and TNT powders.

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1. INTRODUCTION

The use of supercritical fluids (SFs) for the analysis, processing, or demilitarization of energetic materials and important related inert ingredients has been under investigation for about the last 10 years. These studies fall into the categories of extraction of propellant stabilizers and plasticizers [1–11], extraction and/or recrystallization of energetic fillers [1,12–18], and extraction of polymers and waxes [19–22]. SFs possess liquid-like densities, gas-like diffusivities and viscosities, and low surface tensions [23]. These properties make SFs attractive as processing solvents. However, as Chester, Pinkerton, and Raynie point out in their recent review article [24], any single-phase fluid, including liquids, may be suitable for carrying out extraction processes.

Figure 1 shows a representative single-component phase diagram. Phase transition equilibrium curves separate the regions of solid, liquid, and gas. Of particular interest is the liquid-gas equilibrium curve, which terminates abruptly at the critical point. The temperature and pressure at the critical point are defined as the critical temperature (T_c) and critical pressure (P_c). An SF results when the temperature and pressure are greater than these critical parameters.
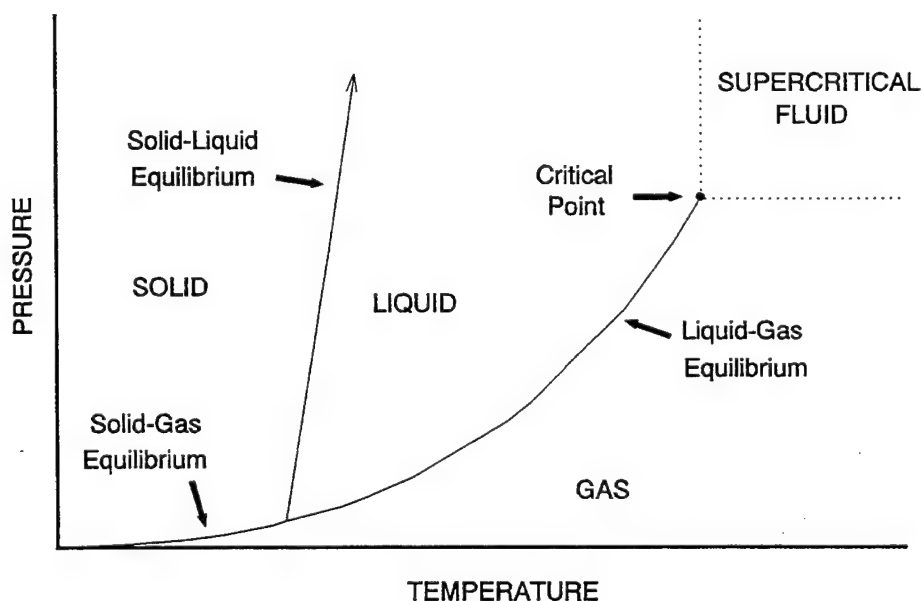

Figure 1. <u>Representative single-component phase diagram.</u>

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One technology developed for demilitarization of energetic materials during the last decade is the U.S. Army Missile Research, Development, and Engineering Center (formerly U.S. Army Missile Command [MICOM]) liquid ammonia process for the recovery of ammonium perchlorate (AP), cyclotrimethylenetrinitramine (RDX), and cyclotetramethylenetetranitramine (HMX) from rocket propellant [25–29]. Results from work done at the U.S. Army Research Laboratory (ARL) indicate that it should also be possible to dissolve and recover RDX from a formulated energetic material by selecting an appropriate polar modifier for supercritical CO_2 [15–18]. However, direct extraction of RDX may not be the preferred route when one considers that RDX is often the primary ingredient in an energetic formulation. It may make more economic sense to extract the secondary ingredients, such as stabilizers, plasticizers, and certain binder ingredients. While mass transfer or diffusion limitations can have a large influence on an extraction process, it is clear that the solubilities of all the chemical components involved need to be considered for solvent selection and process design.

CO_2 is arguably the most environmentally benign solvent known, next to water. CO_2 is not an ozone-depleting substance. While CO_2 is a greenhouse gas, its production can involve a number of natural sources [30], so the capture and use of CO_2 can be thought of as a temporary diversion from its ultimate atmospheric fate. CO_2 is abundant and cheap at 3 cents per pound in bulk.

A large body of literature exists on the use of CO_2 as an extraction solvent [24,31]. The critical parameters for CO_2 are easily accessible, with $T_c = 304.2$ K and $P_c = 7.38$ MPa [30]. The solubility data for RDX in CO_2 are limited, with indications that RDX and HMX are both fairly insoluble in this solvent [1]. In contrast, an extensive set of solubility data for 2,4,6-trinitrotoluene (TNT) in CO_2 have recently been reported by a group at the Fraunhofer Institut für Chemische Technologie (ICT) [32]. As will be seen below, TNT is up to 3 orders of magnitude more soluble in CO_2 than is RDX.

2. EXPERIMENTAL

The equipment used to determine the solubility of RDX in supercritical CO_2 is shown in Figure 2. A 260-ml syringe pump (ISCO model 260 D) was filled with neat liquid CO_2. One of the multiport

valves on a small supercritical fluid extraction (SFE) unit (CCS Instrument Systems) was configured to bring a 1-ml extraction vessel online or offline of the CO_2 flow. The extraction vessel was filled with RDX, and the RDX particle size was kept below 150 μm in order to maximize the ratio of surface area to mass, which helps to ensure rapid saturation of the fluid with the solute. A liquid chromatographic multiwavelength ultraviolet-visible (UV-Vis) detector (Thermo Separation Products), equipped with internal light sources and a high-pressure flow cell, was used to detect RDX levels in the fluid. The detector wavelength was set to 246 nm for the solubility measurements. The flow cell and the transfer line from the extraction unit were thermally stabilized using a water circulator. A variable linear restrictor (ISCO) was used to adjust the CO_2 flow rate through the system. As the CO_2 exited the flow restrictor, its pressure dropped to ambient. The resulting gas was bubbled through acetonitrile in a collection flask, where the RDX that was initially dissolved in the CO_2 would be trapped.

The experimental setup was modified for detector calibration, as shown in Figure 3. A transfer line with a 2-ml sample injection loop was connected between the syringe pump and the flow cell on the UV-Vis detector, and the variable restrictor was removed. The detector was put into scan mode over a range of 200–400 nm with 1-nm resolution. The syringe pump was filled with acetonitrile and was set to a constant flow rate of 0.5 ml/min.

The sample injection loop was filled with calibration standards of RDX in acetonitrile. The sample loop was brought online, and spectra of each calibration standard were recorded. Spectra from the three most dilute calibration standards (20–80 mg RDX/l acetonitrile) were averaged. The original experimental setup was restored, and seven spectra of RDX in supercritical CO_2 were taken over a range of 308–353 K and 20–40 MPa. These spectra were examined for variations in the RDX
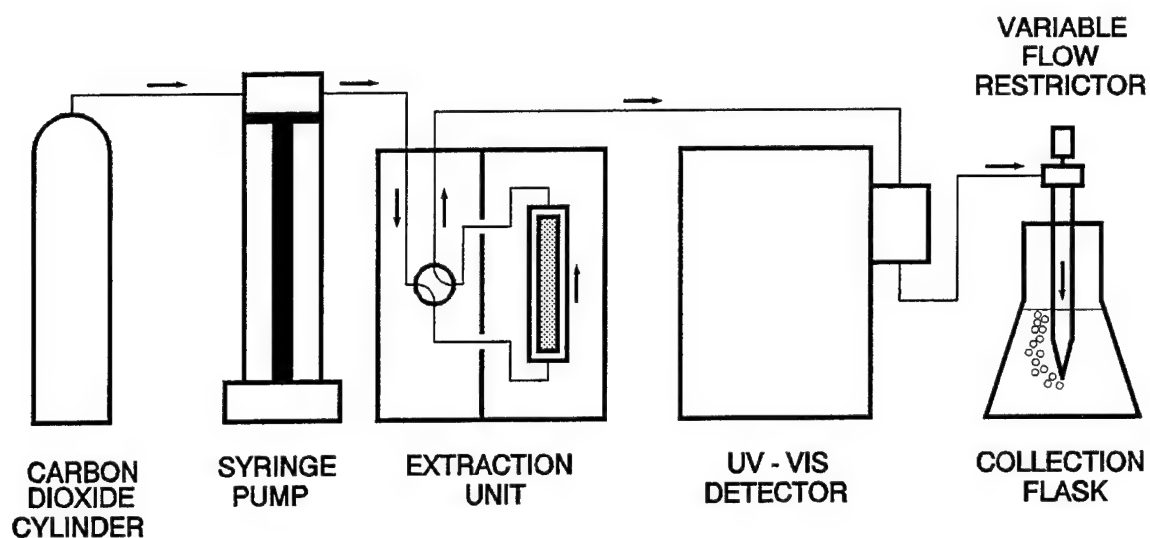
Figure 2. Apparatus for measurement of RDX solubility in supercritical CO_2. The drawing of the extraction unit shows the multiport valve and the extraction vessel that is filled with RDX.
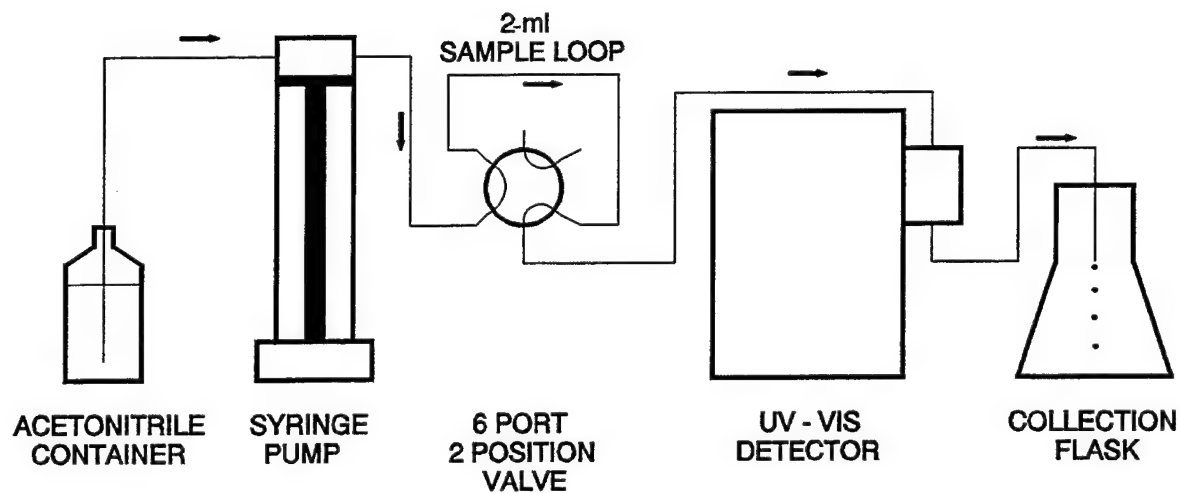

Figure 3. Apparatus for calibration of the UV-Vis detector.

absorption peak shape, width, and maximum in the range of 220–300 nm. The lack of significant variations in peak shape and position over the temperature and pressure range of these seven spectra indicate that RDX is probably not subject to the type of density-dependent changes in molar absorptivity that have been reported for anthracene and pyrene solutes in CO_2 [33]. The seven spectra taken in supercritical CO_2 were averaged for comparison with the spectra taken in acetonitrile. The averaged spectra of RDX in acetonitrile and RDX in supercritical CO_2 are shown in Figure 4. These averaged spectra are normalized to the peak maximum of the lowest energy UV transition that occurs in the range of 220–300 nm.

In order to use the acetonitrile calibration standards to determine the concentration of RDX in the 250-nl detector volume, the two averaged spectra for RDX dissolved in acetonitrile and RDX dissolved in supercritical CO_2 need to be superimposable in the wavelength region where the UV absorption measurements are made, using only a linear shift of the wavelength scale. A good empirical match is observed between the averaged spectra of RDX in supercritical CO_2 and an 8-nm blueshift of the averaged spectra of RDX in acetonitrile in the range of 220–300 nm. The UV absorbance data for RDX in CO_2, which was collected at 246 nm, was calibrated using the RDX standards in acetonitrile at 254 nm. A Beer's Law plot of the absorbance at 254 nm of RDX in acetonitrile was found to be linear over the entire range of standards.

A typical RDX solubility profile in CO_2 is shown in Figure 5. A UV absorbance baseline was established by collecting data with the extraction vessel offline, allowing RDX-free CO_2 to flow through the detector. After 10 min, the extraction vessel was put online, allowing CO_2 to flow through it and saturate with RDX.

Equilibration typically occurred within several min after placing the extraction vessel online. The variable restrictor was adjusted to keep the flow rate of liquid CO_2 measured at the pump around 0.5 ml/min or less. The actual flow of supercritical CO_2 was somewhat higher, as determined by the ratio of CO_2 density in the liquid and supercritical states at the same pressure but
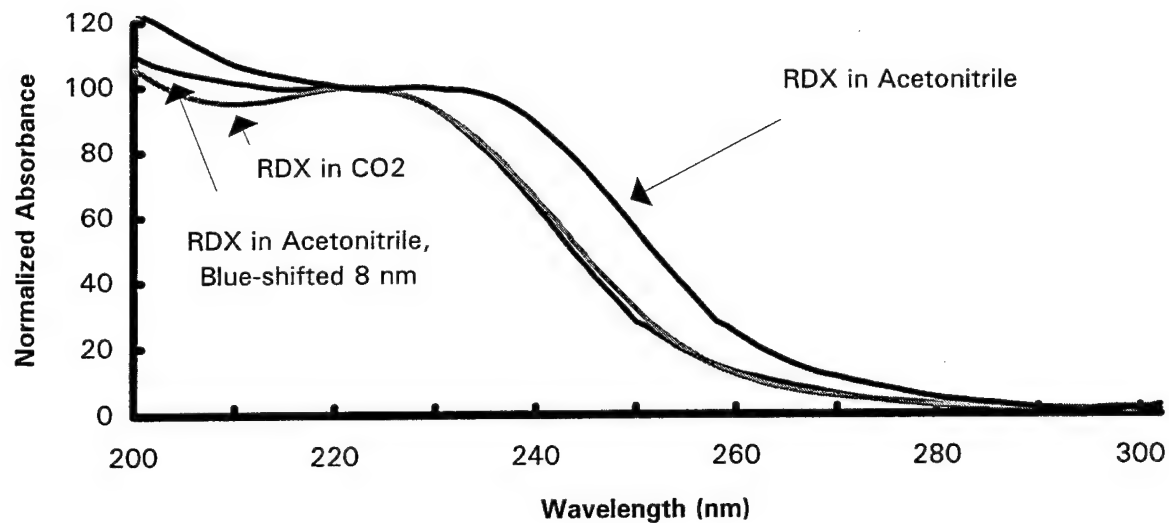
Figure 4. Spectral shift of RDX in CO_2 relative to RDX in acetonitrile calibration solutions.
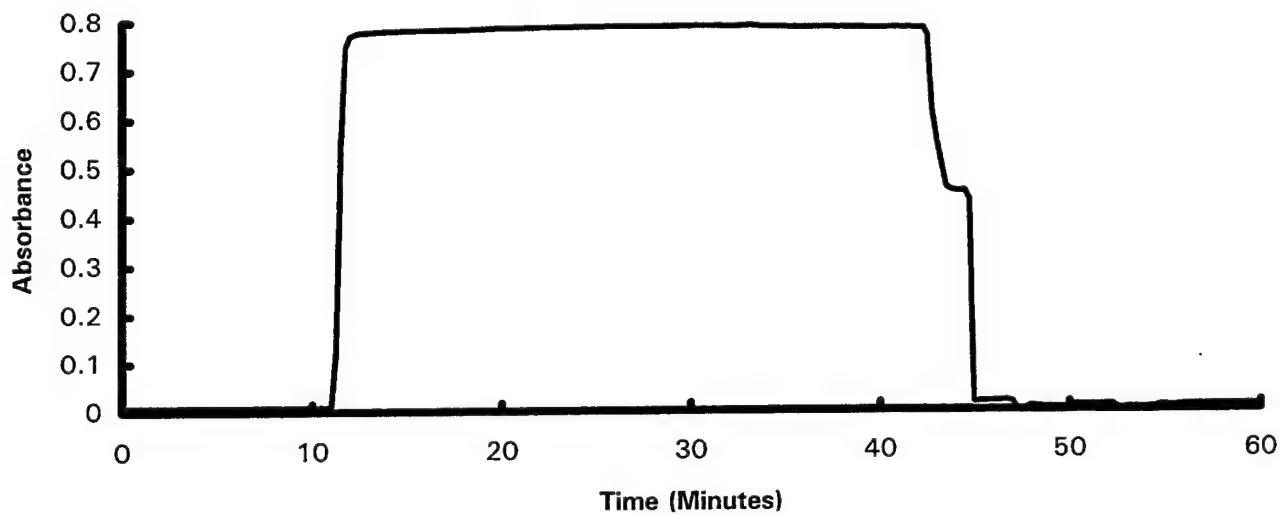

Figure 5. Typical RDX solubility profile in CO_2 at 246 nm. The extraction vessel was put online at 10 min.

different temperatures. Equilibration of the solubility measurement was checked at 323 K and 41.4 MPa by repeating the solubility measurement at different CO_2 flow rates. The solubility measurement was found to be independent of flow rate over the range of 0.2 ml/min to 1.8 ml/min at 323 K and 41.4 MPa, indicating that the SF was saturated with solute. If the fluid was not saturated with solute at the higher flow rates, an increase in solute concentration would have been observed at lower flow rates, due to the longer residence time of the fluid through the extraction vessel.

The net RDX absorbance for each run was determined by subtracting the average baseline level from the average RDX level after the system equilibrated. This absorbance measurement was converted into an RDX concentration per volume (milligrams RDX/milliliter fluid) by using the detector calibration determined with the acetonitrile standards at 254 nm. The CO_2 density in the detector flow cell was then used to determine the RDX concentration per mass CO_2 (milligrams RDX/gram CO_2), which was subsequently converted into an RDX solubility mole fraction. This technique of flowing CO_2 through a vessel filled with solute and determining the mass of sample dissolved is an example of a dynamic solubility determination [34].

3. RESULTS AND DISCUSSION

3.1 <u>RDX Solubility in CO_2</u>. Measurements of the solubility of RDX in CO_2 were made at the temperatures and pressures indicated in Table 1. It should be pointed out that CO_2 is not supercritical at 303 K or 6.9 MPa. Unless otherwise indicated in Table 1, only a single measurement was made at each set of temperature and pressure conditions. The only set of conditions from which enough solubility measurements were made to get a meaningful error estimate (1 standard deviation) was at 323 K and 41.4 MPa. Under these conditions, the solubility was determined to be 0.097 ± 0.009 mg RDX per gram CO_2.

Table 1. Solubility of RDX in CO_2 (Milligrams RDX/Gram CO_2) as a Function of Temperature and Pressure

MPa	303 K	308 K	323 K	338 K	353 K
6.9	0.002	0.000	0.000	—	—
10.4	0.007	0.008	0.003	0.001	—
13.8	0.013	0.013	0.013	0.009	0.004
27.6	0.032	0.034	0.051	0.076	0.114
41.4	0.053	0.067	0.097[a]	0.173	0.237[b]
48.3	0.055	0.064	0.111	0.173	0.254[b]

[a] Average of seven measurements. Error estimate: 0.009 mg RDX/g CO_2.
[b] Average of two measurements.

Bartle et al. [35] outline a fit of solubility data to the following equations:

$$\ln(E) = a + b*\rho \tag{1}$$

$$E = x*P/P_{vap}, \tag{2}$$

where the constants "a" and "b" are fitting parameters, "ρ" is the system density, "x" is the solute (RDX) mole fraction, "P" is the system pressure, and "P_{vap}" is the solute vapor pressure. The quantity "E," defined in equation 2, represents the enhancement of solute concentration in the supercritical phase relative to the concentration based upon its vapor pressure. For dilute solutions, the density of CO_2 can be used to approximate ρ. Since P_{vap} and ρ are both temperature-dependent quantities, equations 1 and 2 are used to make isothermal fits to the solubility data. The fitting parameters can be obtained by calculating E for each condition of temperature and pressure and performing a linear regression on equation 1. The RDX mole fraction data are calculated from the solubility values listed in Table 1. The RDX vapor pressure data of Dionne et al. [36] used to make these fits are listed in Table 2. CO_2 density values were obtained using the ISCO computer program SF-Solver [37]. Figure 6 shows a plot of these calculated CO_2 density values as a function of

temperature and pressure. The resulting fitting parameters are listed in Table 2. Equations 1 and 2 can be rewritten as:

$$x = (P_{vap}/P) \exp(a + b*\rho). \tag{3}$$

Figure 7 shows the fit of equation 3 to the RDX mole fraction data in CO_2.

Table 2. RDX Vapor Pressure[a] (P_{vap}) and Fitting Parameters for RDX Solubility in CO_2

	303 K	308 K	323 K	338 K	353 K
P_{vap} (MPa)	1.42×10^{-12}	3.16×10^{-12}	2.98×10^{-11}	2.31×10^{-10}	1.50×10^{-9}
a	3.976	4.509	6.003	6.705	4.701
b (m^3/kg)	0.01545	0.01452	0.01163	0.00994	0.01122

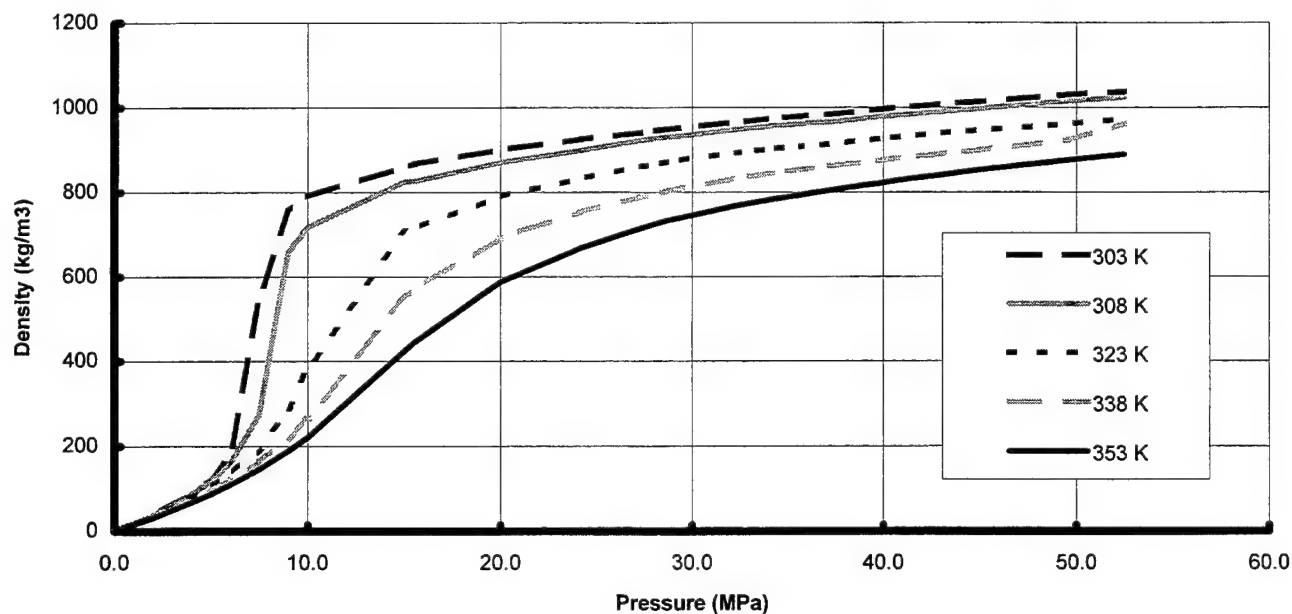[a] See Dionne et al. [36].

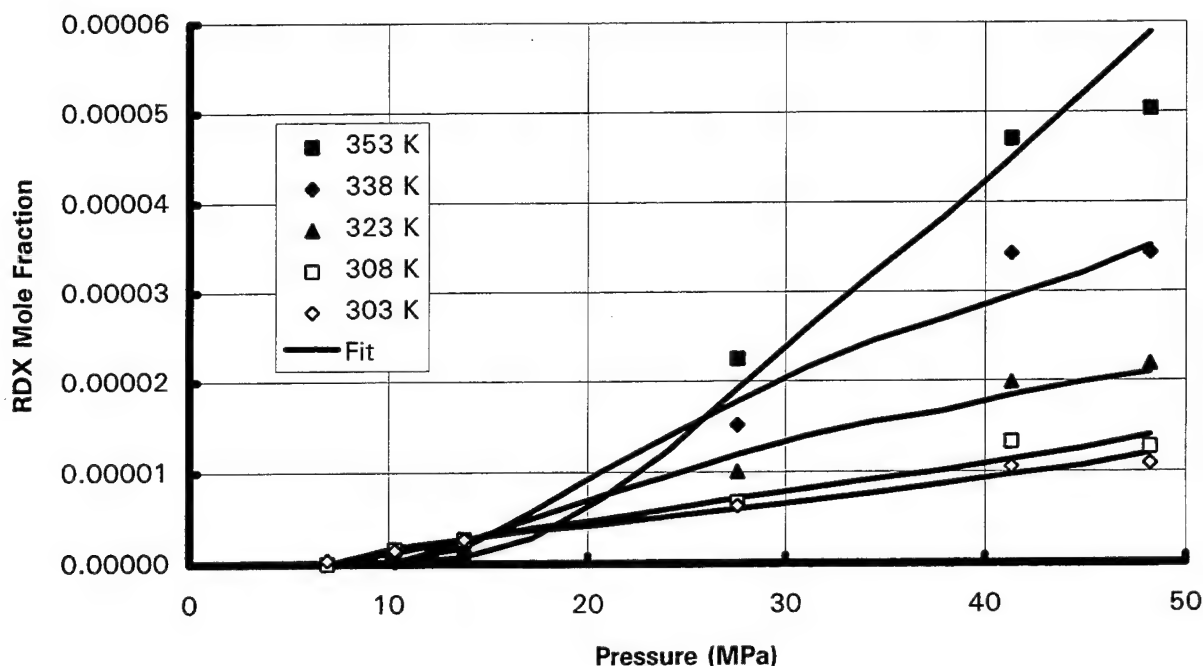Figure 6. Density of CO_2 as a function of temperature and pressure.

Figure 7. <u>RDX mole fraction in CO_2 as a function of temperature and pressure.</u>

The form of the solubility isotherms shown in Figure 7 is typical of most materials. Solubility isotherms for almost 90 low-volatility substances can be found in Bartle et al. [35]. The crossing of the RDX solubility isotherms that occurs in the pressure range of 10–20 MPa is due to competition between two physicochemical properties. Most organic compounds show an increase in solubility in CO_2 at higher pressures and temperatures. From equation 3, it should be clear that the temperature dependence of the solubility is functionally related to the solute vapor pressure and the fluid density. Raising the temperature results in an increase in the RDX vapor pressure (see Table 2) and a decrease in the CO_2 density (see Figure 6). Also, the vapor pressure occurs as a linear term in equation 3, while the density occurs within an exponential term. At lower pressures, the effect due to the decrease in CO_2 density as the temperature is raised is greater than that due to the increase in solute vapor pressure, resulting in lower solubilities. When the pressure is raised high enough, the decrease in CO_2 density with increasing temperature is less than that observed at lower pressures, and raising the temperature results in an increase in solubility, as can be seen in the highest pressure region in Figure 7.

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3.2 <u>TNT Solubility in CO_2.</u> The solubility of TNT in CO_2 was also investigated at the ARL. Measurements were made using the experimental setup shown in Figure 2, with the exception that the UV-Vis detector was not used. TNT was found to be so soluble in CO_2 that the UV absorbance of the solution exhibited severe nonlinear deviations from Beer's Law due to the high TNT concentration. As an alternative means to determine the mass of TNT dissolved in the CO_2, following each run the acetonitrile solution in the collection flask was analyzed via high-performance liquid chromatography (HPLC) using UV detection at 246 nm. These TNT solubility data are presented in Table 3. Error estimates (one standard deviation) for the measurements made at 293 K are presented in the footnotes to Table 3. These error estimates are substantially larger, on a percentage basis, than those for the online UV-Vis determination of RDX. The main reason for the increase in the uncertainty of the HPLC method is that it is possible to form acetonitrile aerosols as the CO_2 is depressurized in the collection flask. Some of the solute can be trapped and lost in these aerosols.

Table 3. Solubility of TNT in CO_2 (Milligrams TNT/Gram CO_2) as a Function of Temperature and Pressure

MPa	293 K	308 K
13.8	4.9[a]	9.6
37.9	13.3[b]	—

[a] Average of five measurements. Error estimate: 2.5 mg TNT/g CO_2.
[b] Average of five measurements. Error estimate: 5.0 mg TNT/g CO_2.

Shortly after these TNT solubility measurements were begun, an extensive set of data on the solubility of TNT in CO_2 was published by a group of researchers at ICT [32]. The ICT solubility measurements covered a pressure range of 15 to 50 MPa and a temperature range of 303 to 413 K. At the highest combinations of temperature and pressure, the ICT data indicated TNT solubilities in excess of 55 mg/g CO_2. It should be noted that the data in Table 3 are consistent with those published by ICT.

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3.3 <u>Comparison of RDX and TNT Solubilities in CO_2</u>. The RDX and TNT solubility data presented in Table 1, Table 3, and in Teipel, Gerber, and Krause [32] can be used to determine the relative solubility of RDX and TNT in CO_2 as a function of temperature and pressure. Ratios of TNT solubility to RDX solubility, representing the relative potential for CO_2 to selectively extract TNT in the presence of RDX, are presented as a function of temperature and pressure in Table 4.

Table 4. Solubility Ratios of TNT Relative to RDX in CO_2 as a Function of Temperature and Pressure

MPa	303 K	308 K	323 K	338 K	353 K
13.8	—	740	—	—	—
27.6	560	540	380	260	170
41.4	610	520	470	>320	>230
48.3	720	790	>490	>320	>220

TNT was found to be at least 2 orders of magnitude more soluble in CO_2 than RDX for the range of temperatures and pressures reported in Table 4. The relative solubilities of TNT and RDX can be explained by considering two physicochemical properties of these solutes: permanent dipole moment and vapor pressure. Molecular mass is not a consideration since RDX (M = 222) and TNT (M = 227) have nearly identical masses. The dipole moments for RDX [38] and TNT [39] have been determined through ab initio Hartree-Fock self-consistent field calculations to be 1.5 debye for TNT and 6.5 debye for RDX. Keeping in mind the heuristic "like dissolves like," one can see why the less polar TNT molecule would have a greater solubility in CO_2 (permanent dipole moment = 0) than does the highly polar RDX molecule. The fact that either of these molecules is even sparingly soluble in CO_2 can be attributed to the relatively large quadrupole moment of CO_2 that results from its π bonding structure, and the $1/r^8$ dipole-quadrupole potential energy interaction [40].

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Vapor pressure data for TNT and RDX are available in Dionne et al. [36], and are plotted in Figure 8. TNT has a vapor pressure at least 2 orders of magnitude greater than that of RDX over a range of temperatures from 303 to 353 K. The fact that the relative vapor pressures of TNT and RDX track their relative solubilities in CO_2 comes as no great surprise when one considers the functional dependence of the enhancement factor, E, upon vapor pressure in equation 3, although one should bear in mind that the contributions of the fitting parameters "a" and "b" have not been fully considered.

The ability to selectively remove TNT in the presence of RDX was demonstrated on a 50:50 (by mass) mixture of the two explosives. The mixture was prepared by placing powder samples of TNT and RDX in a vial and shaking the vial. The equipment shown in Figure 2 was used, without the UV-Vis detector, to extract the TNT from the mixture. A 292-mg sample of the RDX/TNT mixture was placed in a 7.5-ml extraction vessel and installed in the extraction unit. The extraction was carried out at 323 K and 13.8 MPa using a large excess—210 g—of CO_2. The temperature and pressure for this demonstration were selected arbitrarily, since TNT will be at least 2 orders of magnitude more soluble than RDX over a large range of pressures and temperatures (see Table 4). The mass of CO_2 used represents the entire capacity of the syringe pump. An extraction demonstration using inert materials is best done by packing the materials into an extraction vessel to avoid solvent channeling through the vessel. Given the hazardous nature of TNT and RDX, it is preferable to leave a large amount of dead volume in the vessel. Since the use of an unpacked vessel is not an optimum arrangement from an extraction point of view, the entire volume of the pump was discharged through the extraction vessel to ensure complete removal of TNT from the sample.

HPLC was used to compare the composition of the mixture before extraction to that of the material remaining behind in the extraction vessel following extraction. The resulting chromatograms are shown in Figure 9. The material remaining behind was found to contain less than 1% TNT. Analysis of the recovered TNT revealed that about 2 mg of RDX were also extracted. The quantity of RDX extracted was consistent with the solubility values in Table 1 for the amount of CO_2 used.
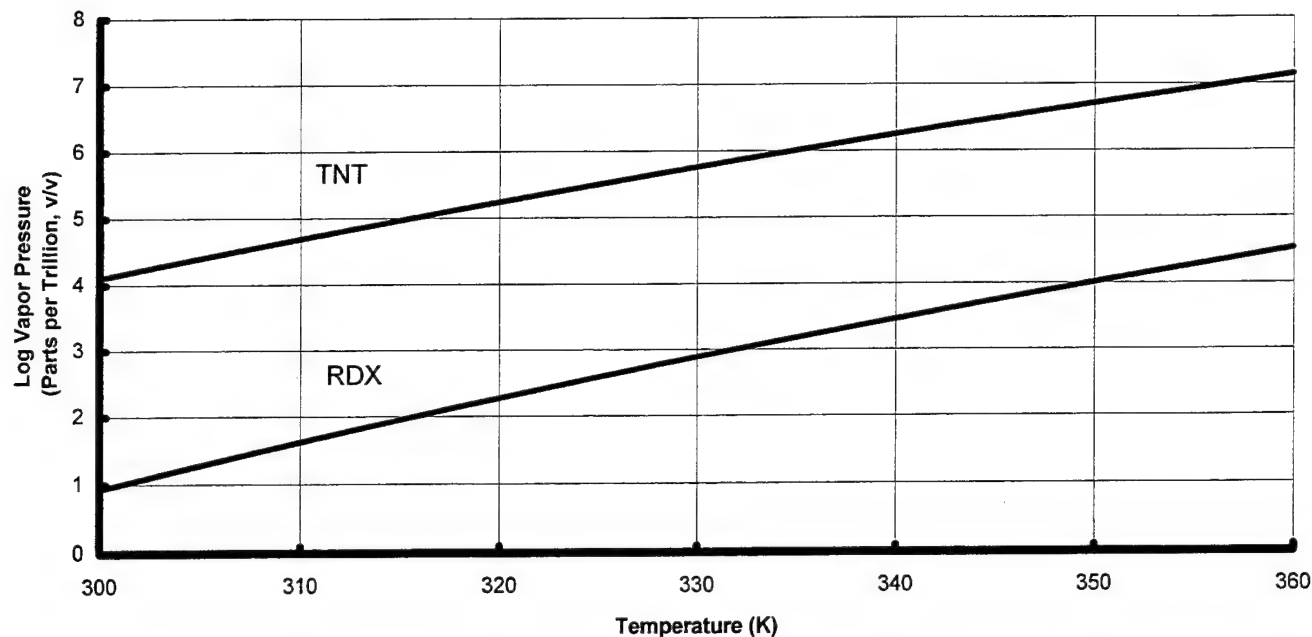
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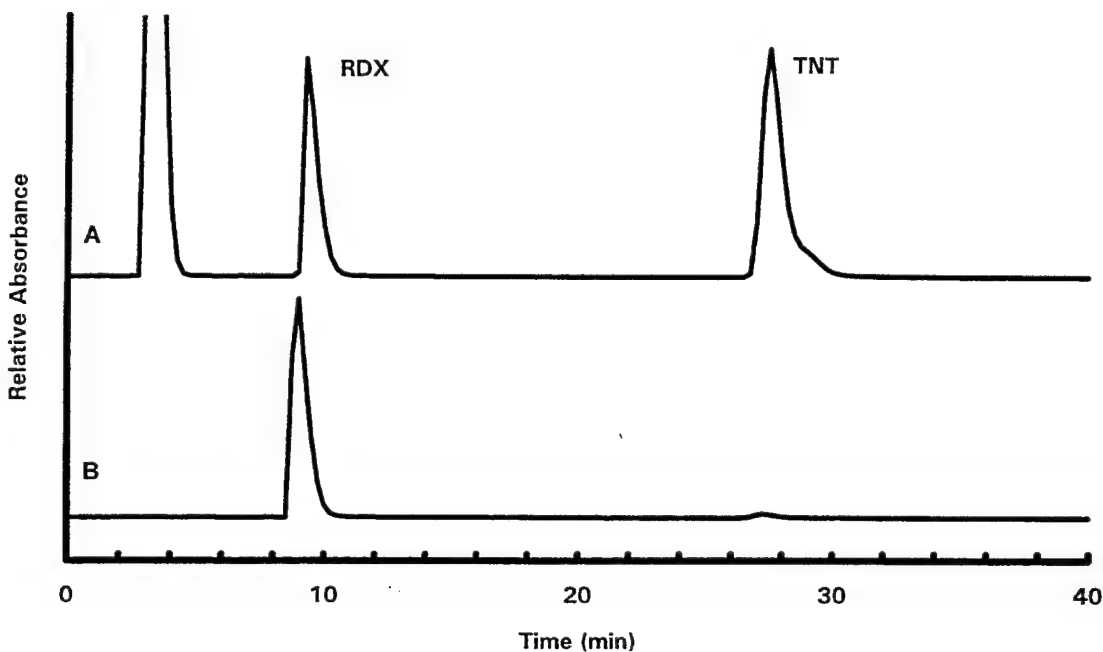Figure 8. Vapor pressures of RDX and TNT, plotted as log (P_{vap}) vs. temperature.

Figure 9. Separation of a mixture of RDX and TNT powders using CO_2 at 323 K and 13.8 MPa: Chromatograms using 246-nm detection of (A) unextracted mixture and (B) recovered material following extraction. The unidentified peak in (A) is due to acetone used to dissolve the sample; acetonitrile was used to dissolve the recovered material in (B).

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4. CONCLUSIONS

This report discusses solubility measurements of RDX and TNT in liquid and supercritical CO_2. While RDX was already known to display limited solubility in CO_2, its solubility was found to vary by over 2 orders of magnitude, depending on the solvent temperature and pressure. It was possible to fit the logarithm of the RDX solubility to a linear function of solvent density under isothermal conditions.

Recently published solubility data for TNT was compared with that of RDX. TNT was found to be 2–3 orders of magnitude more soluble than RDX in supercritical CO_2 over a wide range of temperatures and pressures.

The large differences in solubility in CO_2 displayed by RDX and TNT were used to demonstrate the potential for selective separation of these explosive components. TNT was selectively extracted from a mixture of RDX and TNT powders. Future efforts along these lines will be directed towards the separation of RDX from TNT in formulations such as Composition B.

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13. ABSTRACT (Maximum 200 words)

Mixtures of 2,4,6-trinitrotoluene (TNT) and the nitramines cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX) are used in a variety of high-explosive formulations, such as Composition B (RDX/TNT) or Octol (HMX/TNT). There has been much recent interest in the use of supercritical fluid (SF) CO_2 technologies for the processing and/or demilitarization of energetic materials. The solubility of RDX in neat CO_2 was measured over a temperature and pressure range of 303–353 K (30°–80° C) and 6.9–48.3 MPa (1,000–7,000 lb/in^2) and is presented in this report.

RDX was found to be relatively insoluble in neat CO_2 in the temperature and pressure range studied, with a maximum solubility of about 0.25mg/g of CO_2. Data for TNT solubility in CO_2 have recently been published by a group of researchers at the Fraunhofer Institut für Chemische Technologie. Consideration of the relative solubilities of RDX and TNT in CO_2 suggests that SF extraction (SFE) of TNT should be effective for separation and recovery of nitramine materials from TNT-based energetic formulations. RDX is found to be 2-3 orders of magnitude less soluble than TNT in SF CO_2. An SFE-based separation process is demonstrated on a synthetic mixture of RDX and TNT powders.

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